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Abstract

This paper presents preliminary results of an investigation of the behavior of candidate barrier material for high level nuclear waste storage, Type 304L stainless steel, in tuff repository environmental conditions. Tuff is a densely welded, devitrified, igneous rock common to the proposed repository site at Yucca Mountain, Nevada. The results discussed include: irradiation corrosion tests, U-bend irradiation corrosion tests, slow strain rate tests, and bent beam stress corrosion tests. Results indicate that Type 304L stainless steel shows excellent resistance to general, localized, and stress corrosion under the environmental and microstructural conditions tested so far. The environmental test conditions are 50-100°C J-13 well water (non-saline, near neutral pH, and oxic in nature) and saturated steam at 100°C. Microstructural conditions include solution annealed and long furnace heat treatments to provoke a sensitized structure. However, this particular type of stainless steel may be susceptible to long-term, low-temperature sensitization because of the combination of expected time at elevated temperature and residual stress in the container after emplacement in the repository. Other grades of austenitic stainless steels are reported to be more resistant to low-temperature sensitization. Future work will therefore include more extensive testing of these grades.

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Introduction

Lawrence Livermore National Laboratory (LLNL) is responsible for high-level nuclear waste package development as part of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. This project is part of the Department of Energy's Civilian Radioactive Waste Management (CRWM) Program, and is investigating the suitability of tuffaceous rocks at Yucca Mountain, Nevada for high-level radioactive waste disposal. The waste package effort at LLNL is developing multibarriered packages for safe, permanent disposal in the repository being considered at Yucca Mountain.

The physical, mechanical, and chemical stability of a metal barrier to survive the 300-1000 year containment objective is the paramount technical issue in selecting a suitable container material for geological disposal of high-level nuclear waste. Austenitic stainless steels serve as the reference container materials in the conceptual design for nuclear waste packages for a geological repository in tuff located in Yucca Mountain at the Nevada Test Site. The corrosion resistance of candidate container materials in the anticipated repository environment is the focus of an experimental program to establish a data base on which the final material selection will be made and from which models to project the long-range corrosion performance will be developed. The purpose of this paper is to summarize data obtained in tests conducted over the period March 1983 to August 1984.

Geochemical Environment

The information concerning geochemical environment and waste form has been provided by Oversby.[1, 2] The proposed repository is located in a welded tuff above the static water table in Yucca Mountain. The ambient temperature in the repository horizon is 25-29°C. The rock unit is a densely welded, devitrified tuff with a small percentage of lithophysical cavities. The rock is estimated to contain about 9% water by volume. The repository horizon is fractured with an average fracture density of 0.8 to 3.9 fractures per meter.[3] While water samples have not yet been obtained from the repository horizon, near-by well J-13 produces water which has flowed through the Topopah Spring Member where it lies at lower elevation and is in the saturated zone. The water from J-13 well is taken as a reference water in the repository horizon. The chemical composition of J-13 water is given in Table 1. The water is oxic and contains 5.7 ppm dissolved oxygen. The low concentration of halide ions suggests that the water should not be aggressive toward stainless steels; however the oxidizing nature of the water makes it corrosive toward carbon steels. The low average rainfall at the NTS creates a low downward infiltration rate for water. The downward flux of water at the repository horizon is estimated at less than 1 mm/yr.[4] Thus, the environmental conditions in this unsaturated region are expected to be air and water vapor for much of the containment period.

The current approach to nuclear waste containment is a system of redundant engineered barriers whose function is to contain radionuclides for several centuries. As a minimum, the package is composed of a waste form and a metal container. Some designs call for a second outer metal barrier (an overpack), while others use a packing material (backfill) around the outer metal barrier. The packing material acts to limit flow of water in the package vicinity and to sorb any radionuclides that have migrated through a corroded or otherwise breached metallic barrier. As the environmental conditions in a tuff repository are expected to be rather benign, the reference conceptual design consists of a single metal barrier surrounding the waste form.

Waste Forms and Packages

There are three forms of high level nuclear waste that may go into the tuff repository: (1) spent fuel (SF) from commercial light water nuclear reactors; (2) defense high-level waste (DHLW), which is a borosilicate glass and is manufactured from the high-level liquid radioactive wastes accumulated from defense installations; and (3) commercial high level waste (CHLW), which is also a borosilicate glass containing the high-level fission products from reprocessing of spent fuel.

TABLE 1 Reference Groundwater Composition for Tuff Repository[2] (J-13 Well)

	Concentration (mg/liter)
Sodium	43.6
Potassium	5.1
Magnesium	1.92
Calcium	12.5
Iron	.01
Aluminum	.01
Silicon	27.0
Fluoride	2.3
Chloride	6.8
Bicarbonate	134.0
Sulfate	18.8
Nitrate	9.2

The spent fuel waste form consists of Zircaloy-clad fuel from pressurized water reactors (PWR) and boiling water reactors (BWR). The spent fuel pins vary in dimension for the different reactor types and models, but in general contain UO_2 pellets, fission products, and actinides enclosed in the cladding. The UO_2 fuel pellets undergo physical and chemical changes during irradiation. The products are generally segregations of oxide compounds that have low solubility in UO_2 or elements that are metallic under redox conditions in the fuel. For geological disposal intact fuel assemblies may be packed into canisters or they may be disassembled and the fuel pins repacked into canisters. The heat output of spent fuel depends on the length of time since the fuel was removed from the reactor and the degree of burn-up while in the reactor. The heat output from spent fuel decreases sharply during the first ten years after removal from the reactor due to decay of short-lived fission product isotopes. After ten years, the decay of longer-lived isotopes control heat production, and the heat output decay is slower.

Defense high-level waste (DHLW) results from processing high-level liquid wastes. These are currently stored at three different sites in the United States. The Savannah River site will be the first source of DHLW. The formulation is described by Baxter.[5] For geological disposal, the molten DHLW glass (∿1050°C) is poured into a stainless steel canister. Although a slow pouring process allows the glass to cool before reaching the container, estimates of the glass temperature on contact are about 750°C. Approximately 17 hours are required to fill the 24 inch diameter 10 foot long canister and several additional hours are required to cool the glass casting and canister to ambient temperature. The times at these elevated temperatures may create a sensitized microstructure in the canister which may then be susceptible to localized and stress-assisted forms of corrosion in aqueous environments. This issue will be addressed in detail later in this report. Type 304L stainless steel was selected for the DHLW pour canisters because of its excellent oxidation resistance during the pouring and cooling operations. During the pouring operation, the outside surface of the canister is radioactively contaminated with fine air-borne glass particles. The surface is cleaned by an abrasive process after the pour; a canister material with minimal scale formation is desirable to minimize this burden. The canister is then sealed with a 304L plate which is upset resistance welded to the canister. The low carbon content of this steel should normally impart resistance to developing a sensitized microstructure in the heat affected zone around welds. However, the combination of high deformation strain and the temperatures developed around welds produced by the upset resistance process may favor eventual development of a sensitized microstructure even in low-carbon stainless steel. While further process development is likely, the Savannah River process can be viewed as prototypic for both DHLW and CHLW glasses.

Commercial high level waste (CHLW) forms result from reprocessing of spent commercial reactor fuel in order to separate potentially useful components such as U and Pu from the fission products and higher actinides. At present, there is no operating reprocessing plant for commercial spent fuel in the United States. Borosilicate glass formulations have been developed as part of the national nuclear program. A small inventory of commercial reprocessing waste exists from the West Valley, NY, operation. Present plans call for casting this waste form into a 304L stainless steel pour canister by a process similar to that discussed for the DHLW.

Figure 1 indicates the temperatures measured on the external surface of the side wall of the canister during a simulated DHLW glass pour operation at Savannah River. A maximum of 550°C was measured in this determination, but a good possibility remains that higher temperatures would have developed at the bottom of the canister where thermocouples were not installed. Experiments are currently underway with thermocouples embedded at the bottom of the canister.

304L as Candidate Canister Fabrication Material

Type 304L stainless steel has served as the reference fabrication material for NNWSI canisters. From past engineering experience, this material is expected to have excellent general corrosion resistance in expected repository environmental conditions that are air and steam at temperatures in the range 95-300°C and with the possible intrusion of vadose water at temperatures below 95°C. The characteristics of this vadose water are that it is non-saline, near-neutral pH, and oxic. Austenitic stainless steels typically show low

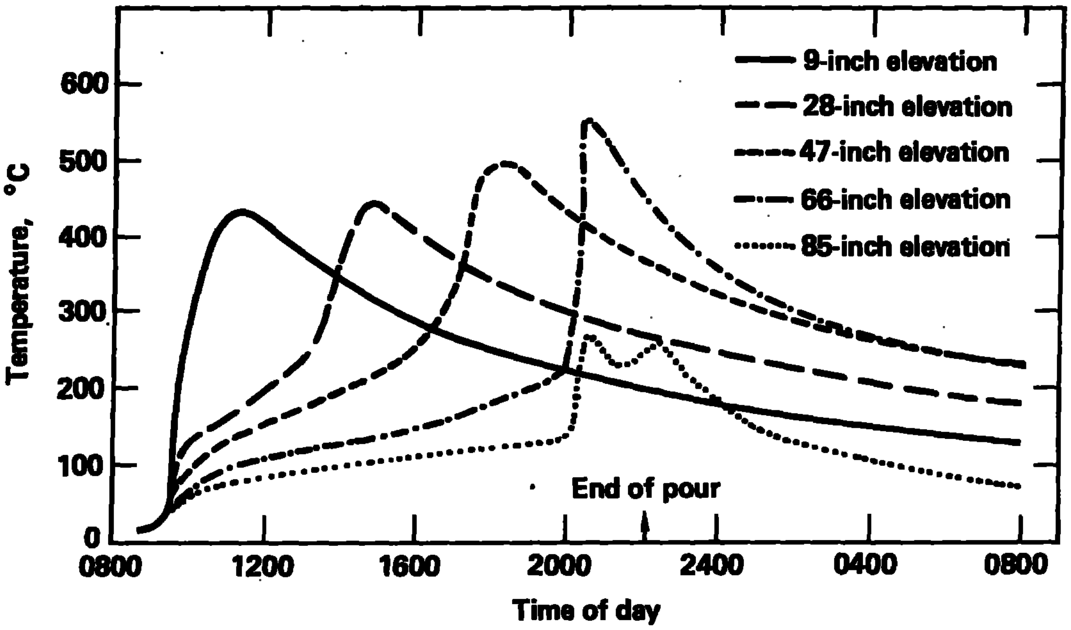

Fig. 1 Cooling curves for full-size canisters filled with glass under reference conditions. These temperatures represent the outside surface of the canister.

general corrosion rates in these kinds of water. A conservative estimate of the wastage of 304L during the containment period (up to 1000 years) shows a loss of 0.1 cm from a canister wall. This estimate was based on "high values" of uniform corrosion and oxidation rates in water, steam, and air assuming linear oxide growth kinetics.[6]

The limiting use conditions of 304L stainless steel are rarely general corrosion wastage, but rather occur by much more rapid penetration via localized or stress-assisted forms of corrosion. The experimental test plan is, therefore, largely aimed at resolving the likelihood of these forms of corrosion occurring during the containment period. For purposes of organization, the forms of corrosion can be placed in two groups: localized and stress-assisted. For a detailed discussion on the potential corrosion-related problems relative to austenitic stainless steel nuclear waste canisters emplaced in a tuff repository, the reader is urged to see reference (7).[7]

Possible Corrosion Degradation Modes of 304L Stainless Steel

The first group of degradation modes deals with corrosion forms favored by concentration of the different chemical species in J-13 water. Fractures in the host rock above the repository could admit episodic surges of water. This water could be retained for some period of time by plugging the fractures below the repository. Contact of the water with the hot canister surface would concentrate electrolytic species by evaporation of water. The chloride-ion concentration is of paramount concern with regard to resistance of stainless steels to localized and stress-assisted forms of corrosion. The other ions present in J-13 water may favor or retard these kinds of corrosive attack. Radiolysis of the aqueous environment can cause chemical changes in the water and the dissolved species which, in turn, influence the form and rate of corrosion. Pitting attack, crevice attack, and transgranular stress corrosion cracking (TGSCC) are corrosion forms that develop on 304L in concentrated electrolytes - particularly in high chloride solutions.

The second group of corrosion degradation modes concern localized and stress-assisted attack favored by a sensitized microstructure. The classical grain boundary chromium depletion mechanism is used to explain sensitization behavior.(8) Sensitization kinetics are typically illustrated using a Time-Temperature-Sensitzation (TTS) curve as shown in Figure 2. While the estimated times and temperatures of DHLW emplacement (17 hours at 750°C) are not with the sensitization regime for "L" grade materials, there are several environmental variables which could contribute to a sensitized microstructure. These will be taken up later in this paper.

The TTS curve represents an isothermal plot, i.e., a behavior which occurs when a sample is held at a constant temperature for a given length of time. The possible sensitization which may occur in the nuclear waste canister does not occur via such an isothermal process, but rather through a complex thermal history including fabrication, glass pouring (DHLW and CHLW), welding, and long-term storage at elevated temperatures.

At low temperatures, below the precipitation region of Figure 2, isothermal carbide precipitation does not occur because of the rapid decrease in the rate of nucleation with temperature. The carbide particles, thermodynamically stable if formed at high temperatures, do not dissolve at lower temperatures. At temperatures too low for carbide nucleation, however, existing particles can continue to grow and establish a new and lower interfacial chromium level as well as a new depletion profile. Such a situation has been shown to occur by Fox (aka Povich) and others(8-11) and will be discussed later in this paper.

During the welding and glass pouring processes (DHLW and CHLW), carbide precipitation may occur (especially in the higher carbon grades, e.g., 304) in both the weld heat affected zone (HAZ) and in the base metal. Since cooling is rapid, these carbide particles remain quite small. Such carbides cause little chromium depletion or sensitization and virtually no degradation in corrosion resistance. Once nucleated however, these carbides are stable and can, as stated above, grow at temperatures where isothermal precipitation

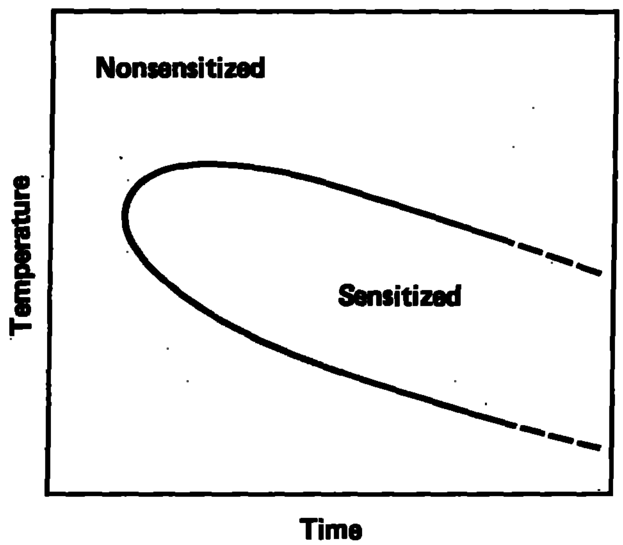

Fig. 2 Schematic time, temperature, sensitization (TTS) diagram

could not occur. Carbide growth is slow and may take several years at storage temperatures of $\sim$200°C. A containment period of 300-1000 years is the objective for the metal barrier causing a great deal of concern about long-term microstructural stability.

Low Temperature Sensitization

While experimental results on specimens given deliberate treatments to try and produce a sensitized microstructure indicate that 304L is thus far resistant to IGSCC, it is well known that three conditions react synergistically to produce this phenomenon in stainless steels: (1) tensile stress, (2) an environment that will facilitate IGSCC (usually mildly to strongly oxidizing), (3) a continuously sensitized microstructure. The sensitized microstructure is produced at high temperature where chromium diffusion is facilitated. For this reason, IGSCC is typically associated with some type of elevated temperature exposure. The glass pouring and welding processes could certainly provide a suitable thermal environment for sensitization although the time at temperature may be insufficient for grain boundary carbide growth and chromium depletion. Lowering the carbon content, as in 304L, avoids "high temperature" sensitization by reducing the chromium carbide particles beyond detectable size limits and breaking up any continuous chromium depleted pathways along grain boundaries.

Preliminary stress analyses show the filled canister to be free of any sizable stresses which would threaten the integrity of the structure. All stress analyses thus far have been quite simple and by no means provide enough information for material selection. However, residual stresses due to cooling of the borosilicate glass and thermal cycling from the closure weld could provide the minimum threshold stress requirement for some type of stress-assisted corrosion.

As mentioned earlier in this paper, the highly fractured tuff rock could experience episodic surges of vadose water which, during the first few hundred years after emplacement, would vaporize upon contact with the canister. The remaining deposits of concentrated electrolytes, particularly chloride ion, could provide initiation sites for localized attack and subsequent propagation as a pit or crack through the container wall.

A sensitized microstructure can be produced in the area to the right of the time-temperature-sensitization (TTS) curve (Figure 2). It has also been shown that sensitization can occur at temperatures below the TTS curve previously believed to be immune to carbide nucleation and growth.[9, 10, 11] This phenomenon is termed low temperature sensitization (LTS).

An example of LTS would be a post-weld stress relief situation. The sensitization that occurs upon welding of stainless steel is usually limited to the heat affected zone (HAZ). Typically, the degree of sensitization due to weld thermal cycles is not appreciable when suitable welding parameters are used. However, sensitization can develop at seemingly "safe" temperatures (<300°C) if chromium carbide nuclei are present, especially in a stress-enhanced situation.

Results of extensive LTS research, detailed in reference 12, show that LTS is a nucleation and growth phenomenon: the chromium carbide particles nucleate in the temperature range 500-800°C and continue to grow at temperatures well below 550°C via substitutional diffusion of chromium and interstitial diffusion of carbon (Figure 3). The rate-limiting growth step would be chromium diffusion in the austenite matrix. LTS has been found to obey an exponential temperature dependence with activation energies ranging from 40 to 70 kcal/mole, depending upon the amount of cold work and on the test method used to measure sensitization. The activation energy of 70 kcal/mole corresponds to diffusion of chromium through the bulk stainless steel and 40 kcal/mole corresponds to chromium diffusion along grain boundaries or dislocation pipes.

The high temperature nucleation of carbides can occur upon welding or any other high temperature exposure. In the case of storage of DHLW and CHLW packages, this high temperature exposure could be produced by welding the canister during fabrication, during glass pouring, or a combination of both.

Computer simulation studies[13] have been developed to predict sensitization and desensitization in a variety of 18 Cr - 8 Ni alloys. These programs are based on classical nucleation theory as well as limited experimental data. Thermal histories representing the glass pouring, welding,

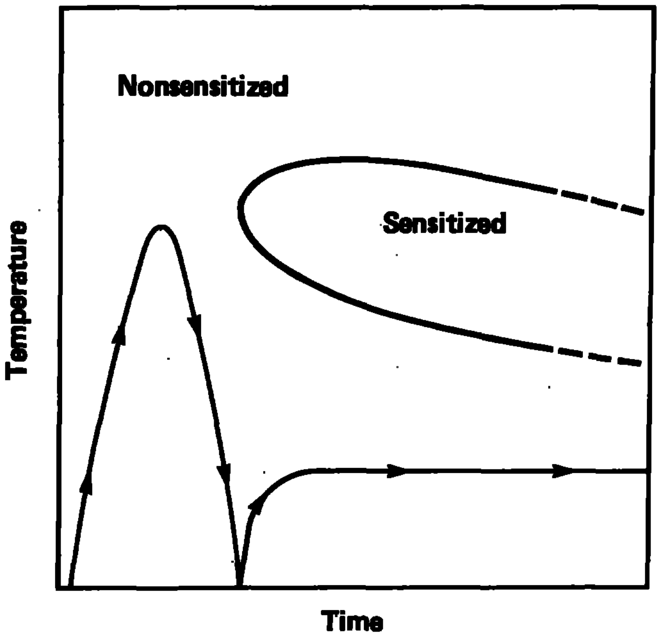

Fig. 3 Low temperature sensitization (LTS) occurs when carbides are nucleated by a brief high temperature exposure followed by holding at temperatures below the TTS curve

and predicted cooling behavior have been generated and in turn superimposed on the computer-generated time-temperature-sensitization curves (TTS). The details of the computer program and the assumptions accompanying the model are available to the reader.[13] An example is shown in Figure 4 using curves generated for Type 304 stainless steel. This of course would yield a more conservative result due to the higher carbon content than 304L. The code predicts no sensitization will occur under the given process time and temperature conditions. Although the author does not state it, the activation energy of 67 kcal/mole for carbide precipitation probably represents bulk diffusion in an annealed material. The activation energy for cold worked material would be significantly lower than that for the annealed case, shifting the "nose" of the TTS curve to the left. Moreover, the present curve does not provide for the LTS phenomenon. Because of high-strain-induced effects, LTS may be operable at conditions outside the precipitation area of the usual TTS curve generated from isothermal treatments which also tend to stress relieve. Computer-simulated sensitization should be altered to accommodate the effects of prior cold work.

Test Program

The purpose of this investigation is to assess the behavior of the 304L reference material in both the stressed and unstressed states in tuff repository environmental conditions and in turn extrapolate these results over the 300-1000 year containment period. In addition to the reference material, a variety of alternative materials is also under investigation. These include 316L, 321, I825, and copper-base materials as an alternative alloy system to the Fe-Ni-Cr alloy system. However this report will deal principally with the results of corrosion testing of 304L and some 304. The 304 data is being reported for comparison. Because it contains more than twice as much carbon as 304L, 304 is much more prone to sensitization than 304L. Type 304 specimens were added to some tests because an early failure of some specimens indicates the test validity to discern susceptibility to non-uniform corrosion modes.

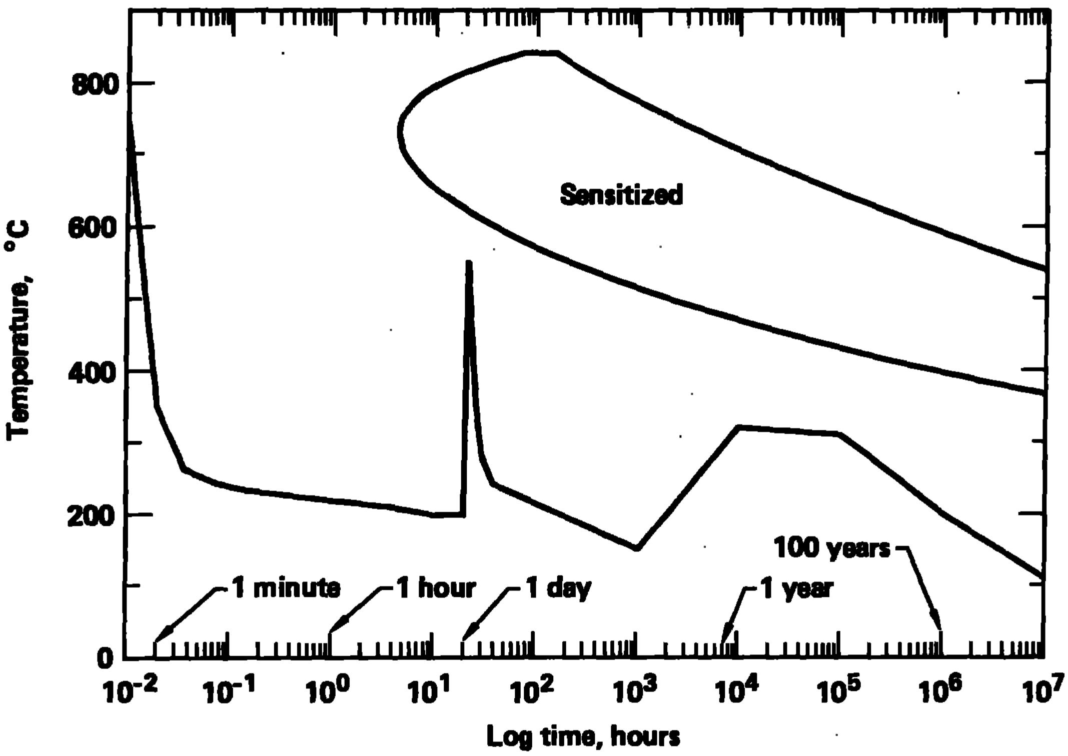

Fig. 4 Computer simulation of Type 304 stainless steel canister. Thermal history showing welding, glass-pouring, and storage.

The test results discussed in this paper include:

(1) Irradiation corrosion tests
(2) U-bend irradiation-corrosion tests
(3) Slow strain rate tests (SSR)
(4) Bent beam stress corrosion tests.

The irradiation corrosion, U-bend irradiation corrosion, and slow strain rate tests were performed at Pacific Northwest Laboratories under the direction of R. E. Westerman and S. Pitman.

Each set of results will be reported separately in the following sections.

1. Irradiation Corrosion Tests

Results are reported on 304L corrosion coupons tested for one year at room temperature and $\sim 1 \times 10^5$ rads/hr in partially aerated (5 ppm O_2) J-13 water in contact with crushed Topopah Spring tuff. This level of gamm flux is based on estimates of the expected dose rate given off by newly emplaced waste. The specimens had been solution annealed and sensitized prior to testing. An identical but non-irradiated test was conducted simultaneously for control. Preliminary chemical analysis of the water after one year of testing indicates that many of the dissolved ionic species in the J-13 water were concentrated by a factor of about two in the irradiated vessel as compared to the unirradiated vessel. The irradiated solution was relatively depleted in dissolved nitrate and oxygen, and enriched in ammonia, chloride, calcium, strontium, magnesium, nickel, and manganese compared to the unirradiated control. It seems probable that the oxygen depletion resulted from an enhanced corrosion rate of the vessel wall which is 304 stainless steel, the soft nickel gasket, or the specimens in the irradiated case, accounting for the higher concentrations of Mn and Ni. However, weight loss measurements on the specimens showed barely detectable corrosion on both the irradiated and non-irradiated material, whether sensitized or annealed.

A summary of the corrosion behavior of the exposed 304L coupons is given in Table 2. Coupons were nominally 1.75-inch diameter rounds 1/16-inch thick. The results indicate a minimal amount of corrosion for both the annealed and for the sensitized material (650°C for 1 hour).

The corrosion test consisted of 24 coupons in each vessel (vessel A-irradiated; vessel B-non-irradiated). The environment within each vessel consisted of J-13 water plus crushed tuff rock in the bottom of the vessel and water at the top. The specimens were arranged so that 12 of them (6 annealed and 6 sensitized) were in water + rock with the remaining 12 (again 6 annealed and 6 sensitized) in water only. The purpose of the water + rock was to embed the specimens in the crushed rock to enhance the possibility of any crevice-induced corrosion attack. The surprising result from the data in Table 2 is that the non-irradiated coupons showed higher corrosion rates than comparable irradiated coupons, although the amount of corrosion penetration was very small in all cases. The sensitizing heat treatment had no effect although as observed metallographically, the degree of sensitization was not very extensive with such short heating times.

2. <u>U-Bend Irradiation-Corrosion Tests</u>.

These tests involve stressed U-bend specimens of 304 and 304L in annealed and annealed-and-sensitized conditions at 50°C and 90°C. The tests are performed in two autoclaves, one at 50°C and one at 90°C, in a ^{60}Co irradiation facility at irradiation intensities of 6 x 10^5 and 3 x 10^5 rad/hr, respectively. Each autoclave is divided into three zones, viz., water + rock (bottom), rock + vapor (middle), and vapor only (top). Each zone contains duplicate U-bend specimens of 304 and 304L stainless steel, in both the solution annealed (15 minutes at 1050°C, air cool) and solution annealed and sensitized (600°C for 24 hrs) conditions. The U-bend specimens are mounted on an alumina rod with alumina spacers, and are insulated from the autoclave by means of a 1-inch wide strip of 30-mil mica sheet located at the non-stressed end of the specimens. With the rack in place, rock chips are added to cover the desired number (16) of specimens, i.e., two-thirds of the total number (24) in the autoclave and J-13 well water is added to cover one-third of the specimens. A temporary Tygon sight tube connected to the inlet fitting at the bottom of the autoclave is used to check the water level. Prior to insertion into the irradiation facility, the autoclaves are operated at full temperature for one or two days to verify the temperature profile. One thermocouple projecting into each of the zones is used for this purpose. Once the proper temperature profile is established, the sight tube

TABLE 2 Corrosion Test Results for Room Temperature Irradiated and Non-Irradiated 304L Coupons (8760 Hrs Exposure)

304L Stainless Steel Material Condition	J-13 Water Environment (28°C)	Corrosion Rates (μm/yr) Vessel A (Irradiated)	Vessel B (Non-Irradiated)
Solution Annealed	Rock + Water	Average: 0.0811*	0.242**
		Range: 0.0690-0.0951	0.215-0.272
		St'd Deviation: 0.00959	0.0201
Solution Annealed	Water	Average: 0.151	0.285
		Range: 0.0817-0.299	0.138-0.451
		St'd Deviation: 0.0734	0.118
Sensitized***	Rock + Water	Average: 0.123	0.249
		Range: 0.111-0.142	0.165-0.322
		St'd Deviation: 0.0114	0.0522
Sensitized	Water	Average: 0.116	0.283
		Range: 0.092-0.142	0.203-0.452
		St'd Deviation: 0.0470	0.0980

* Averages of 6 coupons in each set.

** Maximum localized penetration measured = 0.010 μm in 8760 hours (appx. 1 year).

*** "Sensitizing" heat treatment: 1 hour at 650°C.

is replaced with 0.125-in Inconel feed tubing and the autoclave is inserted into the access tube of the irradiation facility. The autoclaves are refreshed daily with 240 ml of air.

In all cases, the Topopah Spring tuff rock used was nominally 1/4-inch in the major dimension. The fines that resulted from the crushing operation were not discarded and rock chips were removed after each examination. The composition and mechanical properties of the 0.060-inch stainless steel sheet used in the manufacture of the U-bend specimens are presented in Table 3. U-bend specimens are stressed beyond the yield strength of the material. The stress level varies along the bent section and no strength-of-materials formula is available to calculate the stress at a given point, as is the case for a bent beam specimen. The self-loading nature of the U-bend permits its use in the small available working space in the irradiated autoclave.

The U-bend specimens in both the 50°C and the 90°C study have been examined after 3 months exposure. In the 50°C study, two specimen failures have been recorded: one after 1 month of exposure, and one after 3 months of exposure. Both specimens were sensitized 304, located in the vapor-only region of the autoclave. The 90°C study had a number of operational problems during its first month of operation, however these have been remedied and the test is in progress. After one month of exposure, two sensitized 304 specimens, both from the water + rock region, failed. The 3 month exposure inspection showed an additional two failures; both 304, one in the vapor-only region and one in the vapor + rock region of the autoclave. A summary of test results is given in Table 3.

Metallographic examination of the fractured specimens in both the 50°C and the 90°C tests revealed only intergranular stress corrosion cracking (IGSCC). An example is shown in Figure 5. Other than the failures noted, the specimens appeared to be in good condition, with no evidence of pitting or other forms of non-uniform attack.

3. Slow Strain Rate Tests.

In addition to the U-bend tests described above, the SCC resistance of 304L and 304 stainless steels was investigated by means of slow strain rate

TABLE 3 Stress Corrosion Cracking Test Results from U-Bend Specimens Exposed to Irradiated J-13 Water, Crushed Tuff Rock, and Water Vapor. Results After 3 Months Exposure.

No. of Specimens Cracked/No. of Specimens Tested

Material	Environment					
	50°C (6×10^5 rads/hr)			90°C (3×10^5 rads/hr)		
	Rock + Water	Rock + Vapor	Vapor	Rock + Water	Rock + Vapor	Vapor
304	0/4	0/4	2/4	0/4	3/4	1/4
304L	0/4	0/4	0/4	0/4	0/4	0/4

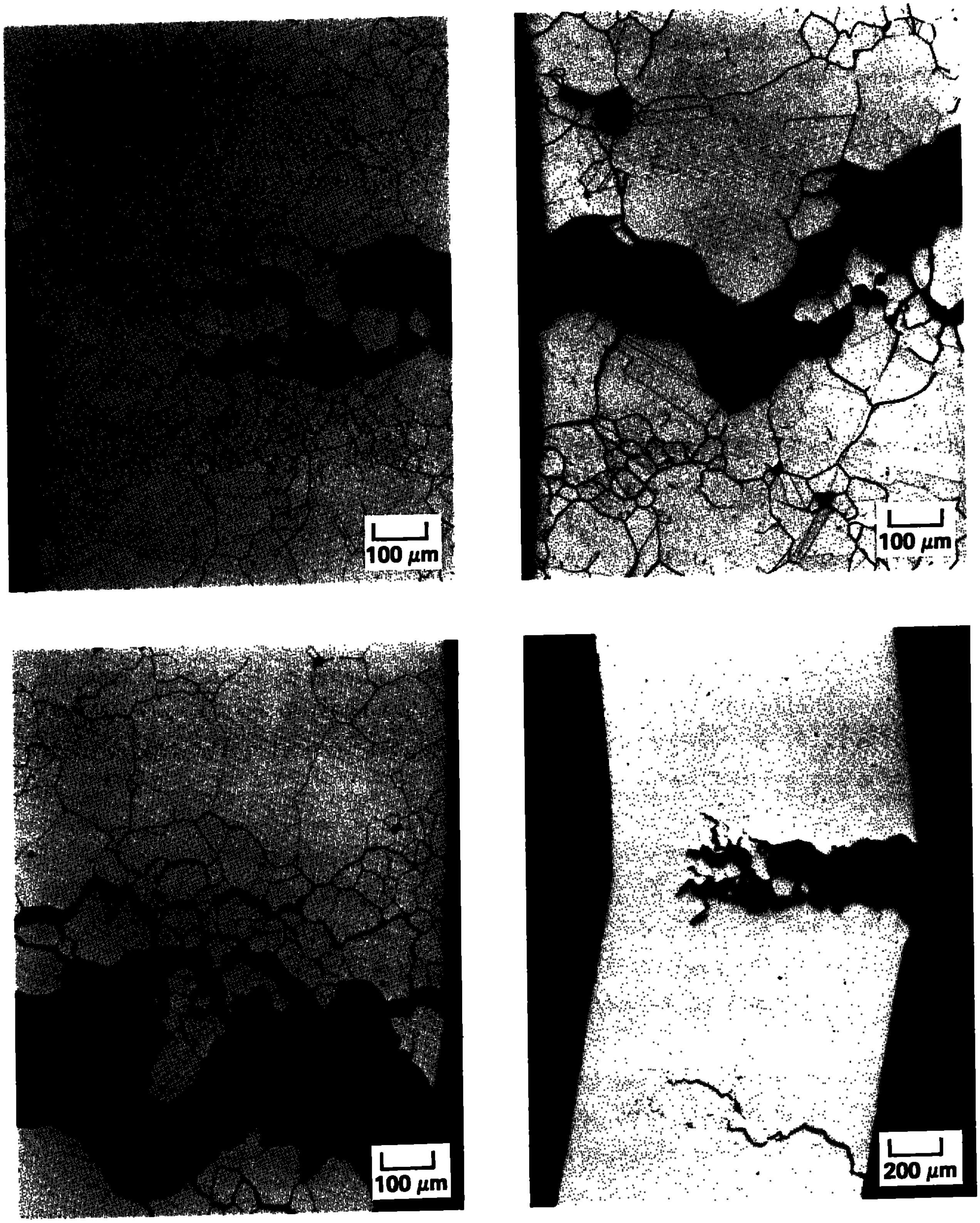

Fig. 5 Metallographic cross-sections of sensitized Type 304 U-Bend specimens showing IGSCC.

(SSR) tests. These tests were performed in air-sparged flowing J-13 well water, with a layer of crushed Topopah Spring tuff rock in the bottom of the autoclave. The water was pumped into the bottom of the autoclave at ∿35 ml/hr on a once-through basis. Control tests were done in air only since gamma irradiation test capability was not yet available at the writing of this paper.

The compositions and mechanical properties of the 304L and 304 are presented in Table 4. The 304 was tested in the mill annealed condition and the solution annealed and sensitized condition (1050°C for 15 minutes, water quench followed by 600°C for 24 hours, air cool). The 304L was tested in two conditions: solution annealed (1050°C for 15 minutes, water quench) and solution annealed with a post annealing sensitization treatment (600°C for 10 hours, air cool). Although 750°C is the measured canister temperature, 600°C was selected to obtain severe sensitization. Because these are preliminary studies, the exact microstructural condition produced by waste emplacement is unknown. Therefore a multitude of microstructures are being examined, beginning with the worst case.

The results of the 304 tests are presented in Table 5. The mill annealed specimens had slightly lower ductility in the groundwater than in air at the low strain rate; however, the changes in ductility were slight and do not indicate a susceptibility to SCC.

The 304 specimens in the solution annealed and sensitized condition failed intergranularly with a significant drop in ductility when the strain rate was reduced from 10^{-4}/s to 1×10^{-7}/s in J-13 well water at 150°C. Cracks were found along the gage section of these specimens and the fracture surfaces showed clear evidence of intergranular fracture.

The results of the 304L tests are summarized in Table 6. Neither the solution annealed nor the solution annealed and sensitized specimens were susceptible to SCC under these test conditions.

TABLE 4 Compositions of Steel Plate Used in Slow Strain Rate Tests

304 STAINLESS STEEL

Alloying Element, percent

N	C	Mn	P	S	Si	Cr	Ni	Mo	Cu	Co
0.0480	0.054	1.44	0.019	0.009	0.39	18.07	8.20	--	--	--

YS: 47.3 ksi (326 MPa)
TS: 89.4 ksi (617 MPa)
El: 57.3%

304L STAINLESS STEEL

Alloying Element, percent

N	C	Mn	P	S	Si	Cr	Ni	Mo	Cu	Co
--	0.024	1.65	0.031	0.012	0.42	18.12	9.52	--	--	--

YS: 42.4 ksi (292 MPa)
TS: 81.1 ksi (559 MPa)
El: 58.5%

TABLE 5 Results of Slow Strain Rate Tests of 304 Stainless Steel at 150°C

Mill Annealed Specimens

Environment	Strain Rate	Reduction of Area, Percent	Elongation Percent	Yield Strength, ksi	Ultimate Strength, ksi
Air	10^{-4}/s	80.2	48.0	37.4	74.4
Air	2×10^{-7}/s	76.5	45.0	35.9	76.6
J-13[1]	10^{-4}/s	77.9	47.0	36.1	75.3
J-13	10^{-4}/s	79.6	46.0	36.3	74.9
J-13	2×10^{-7}/s	75.7	50.0	33.5	77.5
J-13	2×10^{-7}/s	76.4	47.0	35.1	77.0

Solution Annealed and Sensitized Specimens

Environment	Strain Rate	Reduction of Area, Percent	Elongation Percent	Yield Strength, ksi	Ultimate Strength, ksi
Air	10^{-4}/s	72.2	50.6	21.9	68.0
Air	10^{-4}/s	66.5	51.5	26.0	68.8
J-13	10^{-4}/s	75.5	53.5	23.5	68.8
J-13	10^{-4}/s	74.9	51.0	23.5	69.0
J-13	2×10^{-7}/s	50.9	-[2]	22.0	70.1
J-13	2×10^{-7}/s	26.4	-[3]	20.7	64.5

1 Air-sparged J-13 well water.
2 Not determined.
3 Broke at gage mark.

TABLE 6 Results of Slow Strain Rate Tests of 304L Stainless Steel at 150°C

Solution Annealed Specimens

Environment	Strain Rate	Reduction of Area, Percent	Elongation Percent	Yield Strength, ksi	Ultimate Strength, ksi
J-13[1]	10^{-4}/s	80.5	54.0	25.8	68.4
J-13	10^{-4}/s	78.4	52.0	27.1	68.2
J-13	$2x10^{-7}$/s	68.7	48.0	28.4	67.7
J-13	$2x10^{-7}$/s	72.9	46.3	26.7	68.2

Solution Annealed and Sensitized Specimens

Environment	Strain Rate	Reduction of Area, Percent	Elongation Percent	Yield Strength, ksi	Ultimate Strength, ksi
Air	10^{-4}/s	73.7	49.0	29.4	68.6
J-13	10^{-4}/s	72.2	49.6	-[2]	-[2]
J-13	10^{-4}/s	74.8	51.6	29.6	69.1
J-13	$2x10^{-7}$/s	76.0	49.0	26.6	68.8
J-13	$2x10^{-7}$/s	70.4	48.0	27.2	68.8

1 Air-sparged J-13 well water.
2 Not determined.

4. Bent Beam Stress Corrosion Tests.

An assembly of 72 four-point loaded, bent beam specimens (ASTM G-39) was loaded on each of several test fixtures which consist of 4 specimen racks (18 specimens per rack). The test was performed in tuff-conditioned J-13 water at 100°C and in saturated vapor above the water (9 specimens on each rack above the water line and 9 below the water line). The specimens (304L and 304) were stressed to 90% of the room temperature yield strength. The specimens were welded (gas metal arc process, full penetration, some intentional variation of argon, carbon dioxide, and helium in the shielding gas mixture), some given a post-weld anneal, and given a sensitizing treatment (700°C for 8 hours). The specimens were cold-worked 20% (multiple-pass, cross-rolled) to simulate a severe canister fabrication residual stress condition. The test matrix was constructed so that at least 3 replicated specimens of each metallurgical condition are exposed to the water and to the steam. The test conditions and specimen details are indicated in Table 7. An additional 36 specimens were loaded. These specimens were cold worked and welded but were not furnace heat treated. The specimens have been characterized metallographically and the welds have been radiographed. To date (September 1984), none of the bent beam specimens have cracked. The specimens are checked periodically (approximately every 1000 hours) for crack initiation.

Discussion

Coupon Tests (General and Localized Corrosion Susceptibility)

Recent weight loss test results (5000 hours exposure) indicate that 304L stainless steel coupons exhibit very low general corrosion rates in J-13 water in the temperature range 50-100°C.[12] The corrosion penetration rates ranged from 0.025-0.380μm/yr and appeared to be independent of the temperature, in the range tested. These corrosion tests followed ASTM G-1 and G-31 test procedures. Specimens were periodically removed from the test cells for observation and weight loss determinations. The trend of corrosion penetration rates showed a decrease with an increase in time. The tests have now attained more than 7500 exposure hours, with the trend toward the small end of the corrosion rate range.

TABLE 7 Status of Stress Corrosion Cracking Test Results For Four-Point Load, Bent-Beam Specimens Exposed to J-13 Water and Steam and Stress to 90% Yield Stress.

Material and Process Condition	Exposure Hrs	100°C J-13 Water No. Specimens Cracked/ No. Specimens Tested	100°C Steam No. Specimens Cracked/ No. Specimens Tested
304 - CWS*	4016	0/9	0/9
304L - CSW	4016	0/9	0/9
316L - CSW	4016	0/9	0/9
321 - CSW	4016	0/9	0/9
304 - COW*	2000	0/3	0/3
304L - COW	2000	0/3	0/3
316L - COW	2000	0/3	0/3
321 - COW	2000	0/3	0/3

*KEY

C = cold-worked, 20%

S = furnace "sensitized" (700°C for 8 hours)

W = double-pass welded

O = acts as a placeholder for each of the above symbols

Examples: 304L CSW means that the plate or specimen is Type 304L stainless steel in the cold-worked, sensitized and welded condition.

--- 316L COW means that the plate or specimen is Type 316L stainless steel in the cold-worked and welded condition without any furnace heat treatment to produce a "sensitized" structure.

Weight loss tests have also been conducted on 304L and other stainless steel coupons in 100°C saturated steam formed from J-13 water and the measured corrosion penetration rates are in this same range. Similarly the other austenitic alloys (316L, 317L, 321, 347, and 825) also exhibit small corrosion rates under these environmental conditions. The corrosion pattern is uniform with only a slight tarnishing in intentionally creviced areas on the coupons. Electrochemical polarization curves were generated for the candidate stainless steels in J-13 water at different temperatures; analyses of these curves indicates general corrosion rates of the same magnitude as those determined from weight loss measurements. The polarization curves further confirmed the resistance of these materials to pitting and crevice corrosion. These results and test procedures are discussed in detail in Reference 14. A few tests performed in irradiated J-13 water and steam indicate that the general corrosion rate is not affected by the gamma radiation. These results were expected as the low halide content of the J-13 water (7 ppm Cl^-, 3 ppm F^-) should not favor pitting and crevice attack and that the mildly oxidizing environmental condition should favor formation and maintenance of protective passive films on the different stainless steels. The gamma radiation could even enhance the stability of the passive film by making the environment more uniformly oxidizing even in creviced areas. In fact, the one-year room temperature data indicated lower corrosion rates in irradiated J-13 water than in the unirradiated water. More testing in irradiated environment is planned to substantiate this explanation.

Stress Corrosion Test Results

All of the test results obtained to date (September 1984) indicate that 304L stainless steel exhibits resistance to stress corrosion cracking in aerated J-13 well water and in the aerated vapor produced from the J-13 water. The 304L also appears to be resistant to cracking in these environments when irradiated. No cracking has yet been observed on specimens of 304L which have been heavily cold worked, welded, and then furnace heat treated at times and temperatures to favor formation of a sensitized microstructure. The only specimens which have cracked are sensitized 304 U-bend specimens exposed in irradiated J-13 water and vapor. Comparably heat treated and exposed 304L U-bend specimens have not yet cracked after more than

5 months of exposure. The reason for including the sensitized 304 specimens was to force an early failure on a highly intergranular SCC (IGSCC) susceptible material and indicate the test sensitivity for distinguishing between resistant and susceptible material conditions. As long incubation periods may be required before SCC is initiated, especially in the expected relatively benign geochemical and geophysical environment of a tuff repository, the SCC tests will continue for considerably longer exposure periods.

Factors Which May Contribute to LTS

The long-term low-temperature exposure of the canisters will come from two sources: the natural cooling of the glass/waste mixture (DHLW and CHLW) and the continued generation of heat from the radioactive decay of the nuclear waste (all packages). While molten glass has been measured to cool below 300°C within 24 hours, as illustrated in Figure 1, the cooling may be somewhat slower when radioactive glass is present and simultaneously generating heat. Thermal exposures in the temperature range 400-500°C have produced LTS changes in 24 hours. After emplacement in the repository, generation of heat from the waste form combined with the rather poor thermal conductivity of the tuff rock will cause the canister surface temperature to rise. For 10-year old spent fuel, representative canister surface temperatures in the 200-250°C range are expected to develop. (Beside the age of the waste, the power loading, presence or absence of packing material, proximity to other packages, burn-up rate of spent fuel, waste package dimensions, and other factors will determine the actual temperatures). Subsequent cooling of the SF waste packages will be slow, and these canisters will remain at temperatures greater than 100°C for hundreds of years. Low temperature sensitization may therefore develop around the welds in a SF canister because of the residual cold work in the welded areas and the subsequent time-at-temperature developed over the canister surface after emplacement in the repository. Reduction of the canister temperature significantly lengthens the time before incubation of a sensitized microstructure.

The DHLW and CHLW pour canisters may be susceptible to development of a sensitized microstructure largely because of the residual stress resulting (1) from the differential thermal expansion during the glass pouring and cooling and (2) from the high strain rates introduced during the upset resistance welding process to close the filled canister. Because of the lower thermal loading proposed for these waste packages, the expected canister surface temperatures which will develop after the repository emplacement are substantially lower than those for the SF packages. For the DHLW/CHLW packages, the maximum expected canister surface temperatures are on the order of 120-150°C. Overpacking the pour canisters with another stainless steel container reduces the vulnerability of the waste package to premature breaching by stress corrosion cracking along a sensitized microstructure. The outer container can be fabricated to be largely free of residual stress. Some residual stress will remain around the closure weld, but the lower surface temperatures expected to develop on the overpack surface should greatly reduce the possibility of low temperature sensitization.

A review of the literature indicates that type 304L stainless steel is susceptible to sensitization and LTS. Further, cold work plays an important role in determining the rate of LTS. The work of C. L. Briant, reported in Reference 15, shows that when specimens are stressed to near their ultimate tensile strength, no high temperature carbide-nucleating heat treatment was needed for LTS to occur. Although this amount of cold work is high in terms of the expected bulk deformation of nuclear waste canisters, it is possible to introduce a thin surface layer of cold work due to grinding or grit blasting. Moreover, some type of "abrasive cleaning" process is planned in the DHLW process to remove molten glass from the outside surface of the pour canister. While no comprehensive studies have been performed on the quantitative relationship between cold work and subsequent rate of LTS, severe cold work has been observed to bring about LTS-enhanced susceptibility to corrosion within the times and temperatures associated with the initial stages of nuclear waste storage. In addition, post-weld stress relief would increase the likelihood of carbide growth even before the glass-pouring operation.

Alternative Materials to 304L

Significant improvements in the long term resistance to sensitization, LTS, and corrosion can be achieved by modification of alloy composition and

*L = low carbon; N = high nitrogen.

fabrication. Compositional changes within the family of austenitic stainless steels is quite reasonable. Type 316LN* is an attractive candidate for several reasons. Localized martensitic transformations can be suppressed by adding molybdenum to austenitic stainless steels. This is highly important in view of the fact that carbon solubility is lower in martensite than in austenite. Thus, a martensitic transformation allows more carbon to become available for chromium carbide formation and subsequent sensitization to occur. Of importance during the expected time-temperature conditions developed after waste emplacement, nitrogen additions provide a poisoning effect on carbide precipitation by interfering with carbon diffusion. Over longer times, once the canister is relatively cool, nitrogen provides added strength. In addition, secondary phases which precipitate at elevated temperatures, e.g., laves, z-phase, and Chi phase, contain no nitrogen and would thus be no more likely to form than in Type 304L.[14] The lowest possible carbon content is always desirable when sufficient nitrogen is available to stabilize the austenitic structure.

Regardless of the material finally selected for nuclear waste containers, homogeneity of the material is of concern.. For example, banding or ferrite stringers in the original ingot could result in compositional variations in the final canister product which may produce sensitization or phase instability. Tighter process controls and sophisticated melting techniques such as vacuum induction melting (VIM), vacuum arc remelting (VAR), and electroslag remelting (ESR) improve the homogeneity of the material. Process specification aimed at producing a more uniform and homogeneous product will be pursued if future testing indicates tendencies of conventionally produced stainless steels to show localized corrosion attack.

Future Work

Many of the tests reported above (irradiated U-bends, 4-point load bent-beams) will continue to gain additional exposure hours as the initiation phase in stress corrosion cracking is often the slowest step. A complete characterization of the possible degradation of mechanical properties of the reference material in the J-13 well water and steam environment is planned for the future. An overall assessment of material behavior will be obtained using slow strain rate tests, fracture mechanics tests (K_{ISCC}) and possibly low-cycle tension-tension corrosion fatigue tests on pre-cracked specimens, under non-irradiated and some irradiated conditions. The focus of the fracture mechanics tests is to predict crack growth rates under a given set of loading and environmental conditions. Decreasing load tests will be performed to determine K_{ISCC} (the threshold stress intensity above which SCC occurs). In order to develop baseline information, preliminary tests will be run using heavily sensitized material. As a compliment to these tests, a series of constant K tests will be run at various stress intensity levels. This data will be used to generate crack growth rate information over a range of stress intensity levels. A key link between the irradiated and non-irradiated is to determine the change in corrosion potential between the environments and how this potential relates to a "critical" potential above which stress corrosion occurs.

The materials reported herein are well characterized at elevated temperatures by relatively short term tests. The slow strain rate and fracture mechanics tests will focus on material behavior over extended periods of time. This will allow time for potentially harmful microstructural features to manifest themselves under realistic conditions, e.g., 100°C, J-13 water/vapor, and eventually irradiation. For example, the high temperature sigma phase produced during prior heat treatment may embrittle the material enough to cause cracking in the low temperature range. In addition to yield and ultimate strength data, the slow strain rate tests will provide the opportunity to visually determine (via SEM and TEM) whether strain-induced or stress-assisted martensite has formed. High-resolution TEM can reveal sub-micron carbide particles. The fracture mechanics tests will provide slow crack growth studies and crack growth rate data in sensitized material in a J-13 environment. Baseline studies on unsensitized material will also be performed; however, the conservative approach using the sensitized condition will remain the focus of the study. The reason for this is to establish which environmental conditions <u>will</u> cause cracking in the stainless steel and then to determine at what probability level such an environmental conditions would occur. This analysis will form the basis on establishing the population of canisters which would breach in a certain period of time. The values of K_{ISCC} obtained from these tests predict the lowest stress intensity level which will allow stress corrosion cracks to grow in J-13 water or steam. The results of stress analyses may then be compared with K_{ISCC} values determined in the laboratory.

A separate study on high temperature second phase identification will also be conducted. The nucleation and growth of these phases will be correlated with mechanical deformation, prior heat treatment, and alloy composition.

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